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CALCIUM OXIDE and HYDROXIDE

March 1984

Canada

ENVIRONMENTAL AND TECHNICAL INFORMATION FOR PROBLEM SPILLS MANUALS

Environmental and Technical Information for Problem Spills (EnviroTIPS) manuals provide detailed information on chemical substances. This information is intended to assist the reader in designing countermeasures for spills and to assess their impact on the environment. The manual has been reviewed by the Technical Services Branch, Environmental Protection Service, and approved for publication. Approval does not necessarily signify that the contents reflect the views and policies of the Environmental Protection Service. Mention of trade names or commercial products does not constitute endorsement for use.

CALCIUM OXIDE AND HYDROXIDE

ENVIRONMENTAL AND TECHNICAL INFORMATION FOR PROBLEM SPILLS

Technical Services Branch
Environmental Protection Programs Directorate
Environmental Protection Service
Ottawa, Ontario

March 1984

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Cat. No. En 48-10/3-1984E
ISBN 0-662-13154-1
BEAUREGARD PRESS LIMITED

FOREWORD

The Environmental and Technical Information for Problem Spills (EnviroTIPS) manuals were initiated in 1981 to provide comprehensive information on chemicals that are spilled frequently in Canada. The manuals are intended to be used by spill specialists for designing countermeasures for spills and to assess their effects on the environment. The major focus of EnviroTIPS manuals is environmental. The manuals are not intended to be used by first-response personnel because of the length and technical content; a number of manuals intended for first-response use are available. The information presented in this manual was largely obtained from literature review. Efforts were made, both in compilation and in review, to ensure that the information is as correct as possible. Publication of these data does not signify that they are recommended by the Government of Canada, nor by any other group.

ACKNOWLEDGEMENTS

The final version of this manual was prepared by the staff of the Environmental Protection Service who rewrote the text, drafted illustrations and incorporated all comments and additions.

The draft of this manual was prepared under contract with Environment Canada by M.M. Dillon Consulting Engineers and Planners, Concord Scientific Corporation, and Waterloo Engineering Limited. The level of detail present was made possible by the many individuals, organizations and associations who provided technical data and comments throughout the compilation and subsequent review.

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1 SUMMARY

CALCIUM OXIDE (CaO)

White to grey solid with no odour

SYNONYMS

Lime, Quicklime, Unslaked Lime, Calx, High Calcium Lime, Calcia

IDENTIFICATION NUMBERS

UN No. 1910; CAS No. 1305-78-8; OHM-TADS No. 7217370; STCC No. No number required

GRADES & PURITIES

Technical grade, 94.5 to 96.8 percent

Agricultural and construction grades

IMMEDIATE CONCERNS

Fire: Not combustible

Human Health: Corrosive by all routes at elevated exposure levels

Environment: Harmful to aquatic life if pH raised significantly

PHYSICAL PROPERTY DATA

State (15°C, 1 atm): solid
Melting Point: 2,580°C
Flammability: not flammable
Specific Gravity (water=1): 3.25 to 3.38 (20°C)
Solubility (in water): 0.12 g/100 g (0°C)
Behaviour (in water): sinks, reacts violenty, evolving heat
Behaviour (in air): reacts with moisture and CO_2
Odour Threshold: odourless

ENVIRONMENTAL CONCERNS

Aquatic toxicity is a function of alkalinity. Calcium oxide has shown no food chain concentration or bioaccumulation toxicity potential.

HUMAN HEALTH

TLV®: 2 mg/m^3 (dust)
IDLH: 250 mg/m^3

Exposure Effects

Inhalation: Inhalation of dust may cause coughing, sneezing, difficult breathing, and inflammation of respiratory passages

Contact: Caustic irritant to eyes and skin. Causes smarting of skin and first degree burns on short exposure and secondary burns on long exposure. Contact to eyes causes pain, burns, watering. Prolonged exposure may result in ulceration, perforation and blindness

IMMEDIATE ACTION

Spill Control

Restrict access to spill site. Issue warning: "CORROSIVE". Call fire department and notify supplier. Stop the discharge and contain spill, if safe to do so. Avoid contact with solid. Keep contaminated water from entering sewers or watercourses.

Fire Control

Not combustible. Use water in flooding amounts only; foam; dry chemical; halon extinguishing agents; or carbon dioxide to extinguish fires in which calcium oxide is involved.

COUNTERMEASURES

Emergency Control Procedures in/on

Soil: Construct barriers to contain spill. Remove material by manual or mechanical means. Shovel into containers with covers

Water: Contain by damming, water diversion, or natural barriers

NFPA
HAZARD
CLASSIFICATION

CALCIUM HYDROXIDE ($Ca(OH)_2$)

Crystals or soft, white powder with no odour

SYNONYMS

Hydrated Lime, High Calcium Hydrated Lime, Caustic Lime, Calcium Hydrate, Slaked Lime, Lime Water

IDENTIFICATION NUMBERS

UN. No. NA9098; CAS No. 1305-62-0; OHM-TADS No. 7216628; STCC No. No number required

GRADES & PURITIES

Technical, 73.7 percent CaO

Agricultural, 65 to 71 percent CaO

Chemical, 71 to 73 percent CaO

IMMEDIATE CONCERNS

Fire: Not combustible. Material can decompose to produce calcium oxide

Human Health: Mildly corrosive by all routes

Environment: Harmful to aquatic life

PHYSICAL PROPERTY DATA

State (15°C, 1 atm): solid
Melting Point: decomposes at 580°C
Flammability: not flammable
Specific Gravity (water=1): 2.24 (20°C)
Solubility (in water): 0.17 g/100 g (0°C)
Behaviour (in water): sinks, no reaction
Behaviour (in air): absorbs carbon dioxide
Odour Threshold: odourless

ENVIRONMENTAL CONCERNS

Aquatic toxicity is a function of alkalinity. Calcium hydroxide has shown no food chain concentration or bioaccumulation toxicity potential.

HUMAN HEALTH

TLV®: 5 mg/m^3 (dust)
IDLH: no value established

Exposure Effects

Inhalation: Inhalation of dust or mist is irritating and damaging to mucous membranes of the upper respiratory tract. Causes difficult breathing, coughing and sneezing

Contact: In the presence of moisture, contact to human tissue is irritating and damaging; excessive skin contact can produce dermatitis. Eye contact causes irritation, burning sensation and possible injury

IMMEDIATE ACTION

Spill Control

Restrict access to spill site. Call fire department and notify supplier. Stop the discharge and contain spill, if safe to do so. Avoid contact with solid. Keep contaminated water from entering sewers or watercourses.

Fire Control

Not combustible. In fire involving calcium hydroxide, water, foam, dry chemical or carbon dioxide may be used.

COUNTERMEASURES

Emergency Control Procedures in/on

Soil: Construct barriers to contain spill. Remove material by manual or mechanical means. Absorb residual liquid with natural or synthetic sorbents. Shovel into containers with covers

Water: Contain by damming, water diversion, or natural barriers. Dredge or vacuum pump to remove contaminants, liquids, and contaminated bottom sediments

2 PHYSICAL AND CHEMICAL DATA

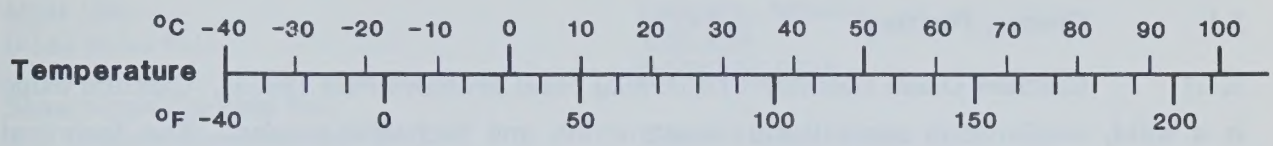
Physical State Properties	Calcium Oxide	Calcium Hydroxide
Appearance	White solid (Patty 1981)	Colourless to white crystalline solid (Patty 1981)
Physical state at 15°C, 1 atm	Solid	Solid
Melting point	2,580°C (CRC 1980)	580°C (-H_2O) (CRC 1980)
Boiling point	2,850°C (CRC 1980)	Decomposes before boiling (CRC 1980)
Decomposition temperature		580°C (Domtar MSDS 1980)
Densities		
Bulk density	960 kg/m^3 (Domtar PDS 1980a)	350 kg/m^3 (Domtar PDS 1980b)
Specific gravity	3.25 to 3.38 (20°C) (CRC 1980)	2.24 (20°C) (CRC 1980)
Fire Properties		
Flammability	Noncombustible but contact with water or moisture may generate sufficient heat to ignite combustible materials (NFPA 1978)	Noncombustible (NFPA 1978) Loses water when heated, forming calcium oxide (Merck 1976)
Decomposition temperature		580°C (Domtar MSDS 1980)
Decomposition products		Calcium oxide and water (Domtar MSDS 1980)
Other Properties		
Molecular weight of pure substance	56.08 (CRC 1980)	74.09 (CRC 1980)

	Calcium Oxide	Calcium Hydroxide
Constituent components of typical commercial grade	94.5% CaO 0.8% MgO 2.5% SiO_2 (Domtar PDS 1980a)	73.7% CaO 0.7% MgO 1.5% SiO_2 (Domtar PDS 1980b)
Refractive index	1.838 (CRC 1980)	1.574 (CRC 1980)
Hygroscopicity	Absorbs carbon dioxide and water from air (Merck 1976)	Absorbs carbon dioxide from air (Merck 1976)
Latent heat of fusion	51.2 kJ/mole (at melting point) (CRC 1980) 79.5 KJ/mole (Lange's Handbook 1979)	
Heat of formation	-635.1 kJ/mole (25°C) (Lange's Handbook 1979)	-986.2 kJ/mole (25°C) (Lange's Handbook 1979)
Heat capacity constant pressure (Cp)	42.1 J/mole•°C (25°C) (Lange's Handbook 1979)	87.5 J/mole•°C (25°C) (Lange's Handbook 1979)
pH of aqueous solution	12.5 (sat'd sol'n) (Patty 1981)	12.5 (sat'd sol'n) (Patty 1981)
Solubility		
In water	0.12 g/100 g (0°C) (Domtar MSDS 1981)	0.17 g/100 g (0°C) (Domtar MSDS 1980)
In other common materials	Soluble in acids (CRC 1980)	Soluble in ammonium salts and acids, insoluble in ethanol (CRC 1981)

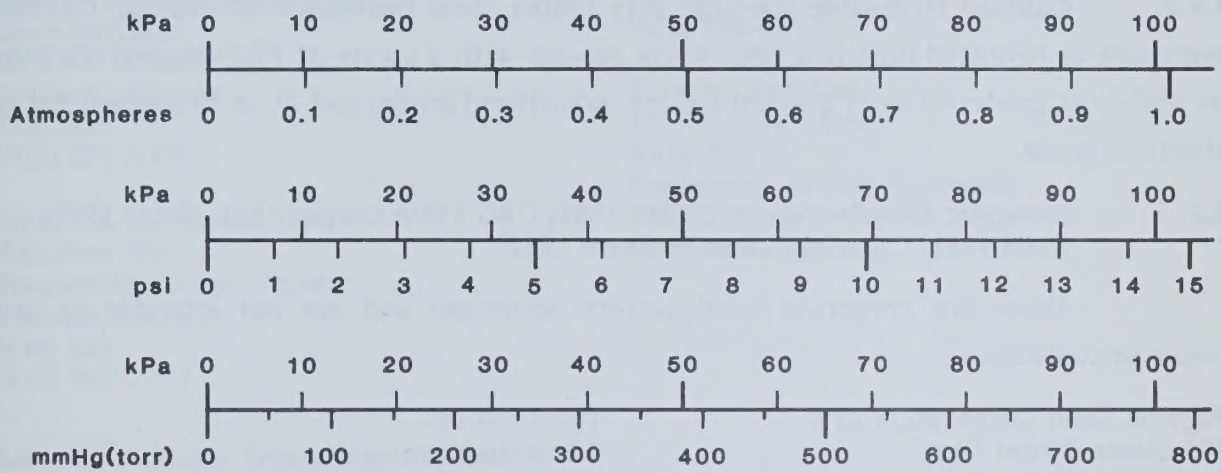
TABLE 1

CALCIUM OXIDE and HYDROXIDE

CONVERSION NOMOGRAMS



Pressure 1 kPa = 1,000 Pa



Viscosity

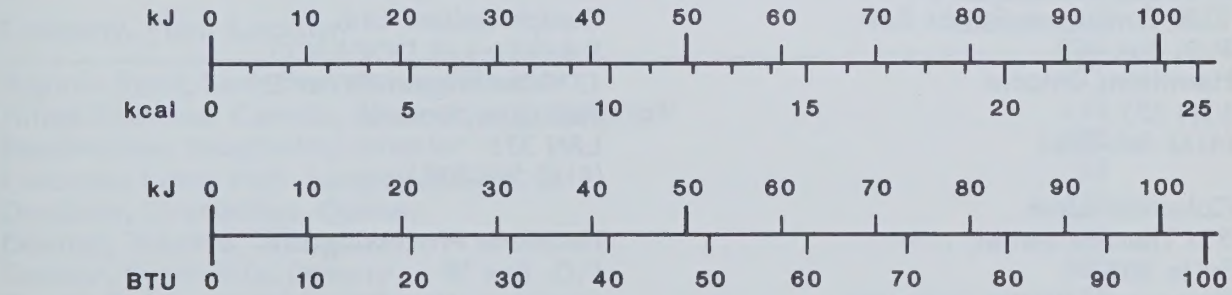
Dynamic 1 Pa·s = 1,000 centipoise (cP)

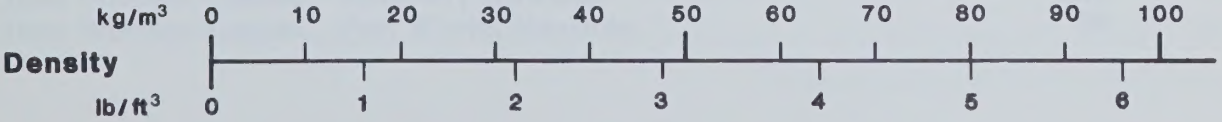
Kinematic 1 m^2/s = 1,000,000 centistokes (cSt)

Concentration (in water)

1 ppm ≅ 1 mg/L

Energy (heat) 1 kJ = 1,000 J





3 COMMERCE AND PRODUCTION

3.1 Grades, Purities

3.1.1 Calcium Oxide (Domtar PDS 1980a; Steel Brothers PDS 1981a). Calcium oxide is a solid, available in agricultural, construction and technical grades. The technical grade has a purity of 94.5 to 96.8 percent.

3.1.2 Calcium Hydroxide (Domtar PDS 1980b; Steel Brothers PDS 1981b). Calcium hydroxide or hydrated lime is a fine, white powder with a purity of 73.7 percent CaO for its technical grade; 65 to 71 percent for its agricultural grade; and 71 to 73 percent for its chemical grade.

3.2 Domestic Manufacturers (CCPA 1981; CBG 1980; Corpus 1981; Scott 1979; CMH 1981; Canadian Lime Institute 1982)

These are corporate headquarters' addresses and are not intended as spill response contacts.

Algoma Steel Corporation Ltd.
503 Queen Street East
Sault Ste. Marie, Ontario
P6A 5P2
(705) 495-3853

Allied Chemical Canada Ltd.
201 City Centre Drive
Mississauga, Ontario
L5B 2T4
(416) 276-9211

Beachvilime Ltd.
Subsidiary of DOFASCO
1330 Burlington Street East
P.O. Box 460
Hamilton, Ontario
L8N 3J5
(416) 544-3761

Columbia Lime
535 Thurlew Street
Suite 303
Vancouver, British Columbia
V6E 3L2
(604) 681-7493

Domlime Inc.
Lime Division
475 Place TransCanada
Longueuil, Quebec
J4G 1P4
(514) 282-5400

Domtar Inc.
C.P. 7212, Succ. A
395 Boul. de Maisonneuve O.
Montreal, Quebec
H3C 3M3
(514) 282-5400

Guelph Dolime Ltd.
Subsidiary of DOFASCO
1330 Burlington Street E
Hamilton, Ontario
L8N 3J5
(416) 544-3761

Havelock Processing Ltd.
P.O. Box 59
Havelock, New Brunswick
EOA 1W0
(506) 534-2311

Reiss Lime Company of Canada Limited
4 King Street West
Toronto, Ontario
M5H 1B6
(416) 865-1991

Shawinigan Carbide Inc.
330 Transmission Avenue
Shawinigan, Quebec

Steel Brothers Canada Ltd.
Lime Division
4836 - 6 Street East
Calgary, Alberta
T2E 3Z9
(403) 276-9335

Steel Co. of Canada Ltd.
P.O. Box 205
Toronto Dominion Centre
Toronto, Ontario
M5K 1J4
(416) 362-2161

Steetley Industries Ltd.
Lime Division
4836 - 6 Street East
Calgary, Alberta
T2E 3Z9
(403) 276-9335

Summit Lime Works Ltd.
P.O. Box 700
Lethbridge, Alberta
TIJ 3Z6
(403) 329-0743

Texada Lime Ltd.
535 Thurlow Street
Suite 303
Vancouver, British Columbia
V6E 3L2
(604) 681-7493

3.3 Major Transportation Routes

Current Canadian production of calcium oxide/hydroxide is widespread, occurring in six out of ten provinces. Ontario produces 77.8 percent of the total, with the largest facilities located in the Woodstock-Ingersoll area. Other major facilities are located near Montreal, Quebec; near Calgary, Alberta; and near Kamloops, B.C.

3.4 Production Levels (Corpus 1981)

Company, Plant Location	Nameplate Capacity kilotonnes/yr (1980)
Algoma Steel, Sault Ste. Marie, Ontario*	275
Allied Chemical Canada, Amherstburg, Ontario*	135
Beachvilime, Beachville, Ontario*	450
Columbia Lime, Fort Langley, B.C.	65
Domlime, Limebridge, Quebec	125
Domtar, Joliette, Quebec	350
Domtar, Beachville, Ontario	560
Guelph Dolime, Guelph, Ontario	65
Havelock Processing, Havelock, N.B.	30
Reiss Lime Canada, Spragge, Ontario	145
Steel Brothers Canada, Faulkner, Manitoba	100
Steel Brothers Canada, Fort Whyte, Manitoba	90

Company, Plant Location	Nameplate Capacity kilotonnes/yr (1980)
Steel Brothers Canada, Kananaskis, Alberta	150
Steel Brothers Canada, Kamloops, B.C.	100
Steel Co. of Canada, Ingersoll, Ontario*	225
Steetley Industries, Dundas, Ontario	125
Summit Lime Works, Hazell, Alberta	50
TOTAL	3040
Domestic Production (1980)	2201
Imports (1980)	41
TOTAL	2242

*Primarily for captive use.

3.5 Manufacture of Calcium Oxide/Hydroxide (Shreve 1977)

3.5.1 General. Calcium oxide is manufactured by calcining calcium carbonate; calcium hydroxide is formed by the hydration of the resulting calcium oxide.

3.5.2 Manufacturing Process (Lime 1980). The mined or quarried limestone is crushed and screened. To "burn" it to calcium oxide, it is loaded into kilns, generally rotary kilns up to 150 m long and 5 m in diameter, and heated to 1,300°C. Calcium oxide is formed by the following reaction:

$$CaCO_3 \longrightarrow CaO + CO_2$$

The calcium oxide is cooled and crushed to the desired size. It may then be hydrated to form calcium hydroxide, a reaction which is described by the following:

$$CaO + H_2O \longrightarrow Ca(OH)_2$$

The calcium hydroxide is clarified in air separators and then packaged.

3.6 Major Uses in Canada (Domtar PDS 1980a, b; Corpus 1981; CMR 1979)

The largest user of calcium oxide/calcium hydroxide is the iron and steel industry. The materials are also used in the pulp and paper industry; in nonferrous smelters; in sugar refineries; in uranium recovery; in cyanide and flotation mills; for water/sewage treatment; in the manufacture of calcium carbide, soda ash, and calcium chloride; for the stabilization of clay soils in highway construction; and in the manufacture of structural blocks and bricks.

3.7 Major Buyers in Canada (Corpus 1981; CBG 1980)

Abitibi-Price, Smooth Rock Falls, Ont.
Abitibi-Price, Jonquière, Que.
Agnew Lake Mines, Agnew Lake, Ont.
Ahlstrom, Moncton, N.B.
Atlas Steels, Welland, Ont.; Tracy, Que.
B.C. Forest Products, Mackenzie, Crofton, B.C.
B.C. Sugar Refining, Vancouver, B.C.
Bethlehem Copper, Highland Valley, B.C.
Boise Cascade, Ft. Frances, Ont.
Burlington Steel, Hamilton, Ont.
Canadian Cellulose, Prince Rupert, B.C.
Canadian Copper Refiners, Montreal, Que.
Canadian Electrolytic Zinc, Valleyfield, Que.
Canadian Forest Products, Port Mellon, B.C.
Canadian Gypsum, Toronto, Ont.
Canadian Int'l Paper, LaTuque, Que.
Canadian Steel Wheel, Montreal, Que.
Cariboo Pulp & Paper, Quesnel, B.C.
Cominco, Kimberley, B.C.
Consolidated-Bathurst, Bathurst, N.B.
Consolidated-Bathurst, New Richmond, B.C.
Consolidated-Bathurst, Trois-Rivieres, Que.
Consumers Glass, Toronto, Ont.
Crestbrook Industries, Skookumchuk, B.C.
Cyanamid Canada, Niagara Falls, Ont.
Denison Mines, Elliot Lake, Ont.
Dofasco, Hamilton, Ont.
Domglas, Montreal, Que.; Bramalea, Ont.
Domtar, Cornwall, Ont.
Domtar, East Angus, Que.
Domtar, Red Rock, Ont.
Donohue St. Felicien, St. Felicien, Que.
Eddy Forest Products, Espanola, Ont.
Eldorado Nuclear, Beaverlodge, Sask.
Enamel & Heating, Sackville, N.B.
Eurocan Pulp & Paper, Kitimat, B.C.
Falconbridge Nickel, Sudbury, Ont.
Fiberglas Canada, Sarnia, Ont.
Granby Mining, Granisle, B.C.
Granduc, Stewart, B.C.
Great Lakes Forest, Thunder Bay, Dryden, Ont.
Griffin Steel, Transcona, Man.; St. Hyacinthe, Que.
Gulf Minerals, Rabbit Lake, Sask.
Inco, Copper Cliff, Ontario; Thompson, Man.
Interprovincial Pipe, Regina, Sask.
Irving Pulp & Paper, Saint John, N.B.
Ivaco, L'Original, Ont.
Johns-Manville Canada, Innisfail, Alta.
Kimberly-Clark, Terrace Bay, Ont.

Lake Ontario Steel, Whitby, Ont.
Manitoba Forestry Resources, Le Pas, Man.
Manitoba Rolling Mills, Selkirk, Man.
Noranda Mines, Rouyn, Que.
Northwood Pulp, Prince George, B.C.
Opemiska Copper, Chapais, Que.
PPG Industries Canada, Toronto, Ont.
Pilkington Glass, Toronto, Ont.
Pine Point Mines, NWT.
Prince Albert Pulp, Prince Albert, Sask.
Proctor & Gamble Cellulose, Grande Prairie, Alta.
Rayonier Canada, Woodfiber, B.C.
Redpath Sugars, Chatham, Ont.
Rio Algom Mines, Elliot Lake, Ont.
St. Lawrence Sugar, Montreal, Que.
St. Regis Alberta, Hinton, Alta.
Scott Maritimes, New Glasgow, N.S.
Shawinigan Carbide Inc., Shawinigan, Quebec
Shefford Chemicals, Granby, Que.
Sidbec-Dosco, Contrecoeur, Que.
Similkameen Mining, Princeton, B.C.
Tahsis, Gold River, B.C.
Texasgulf Canada, Kidd Creek, Ont.
Western Canada Steel, Vancouver, B.C.
Weyerhaeuser Canada, Kamloops, B.C.
Winfield Chemical, Woodstock, N.B.

4 MATERIAL HANDLING AND COMPATIBILITY

4.1 Containers and Transportation Vessels

4.1.1 Bulk Shipment. Calcium oxide and calcium hydroxide are shipped primarily in bulk using covered hopper cars and trucks, or in bags. Typical dimensions and specifications of the hopper cars are given in Figure 1 and Table 2. Commercial hydrated lime is available as a dry powder, while quicklime may be processed to a fine crystalline structure (CLF 1964).

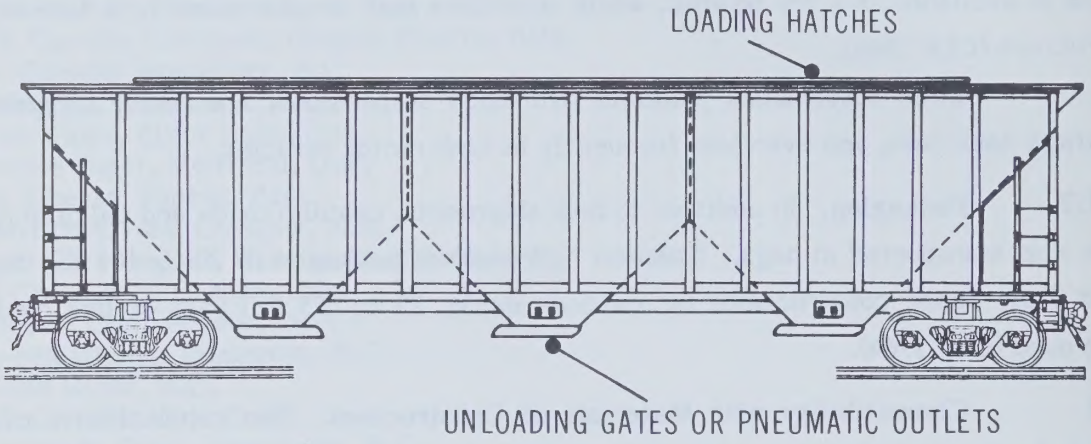
Lime suspensions (calcium hydroxide suspensions) are rarely shipped bulk in railway tank cars, and even less frequently in tank motor vehicles.

4.1.2 Packaging. In addition to bulk shipments, calcium oxide and calcium hydroxide are also transported in bags. Calcium hydroxide is packaged in 20 kg (44 lb.) bags of 2- and 3-ply paper construction; for calcium oxide, 25 kg (55 lb.) bags of like construction are used (CLF 1964).

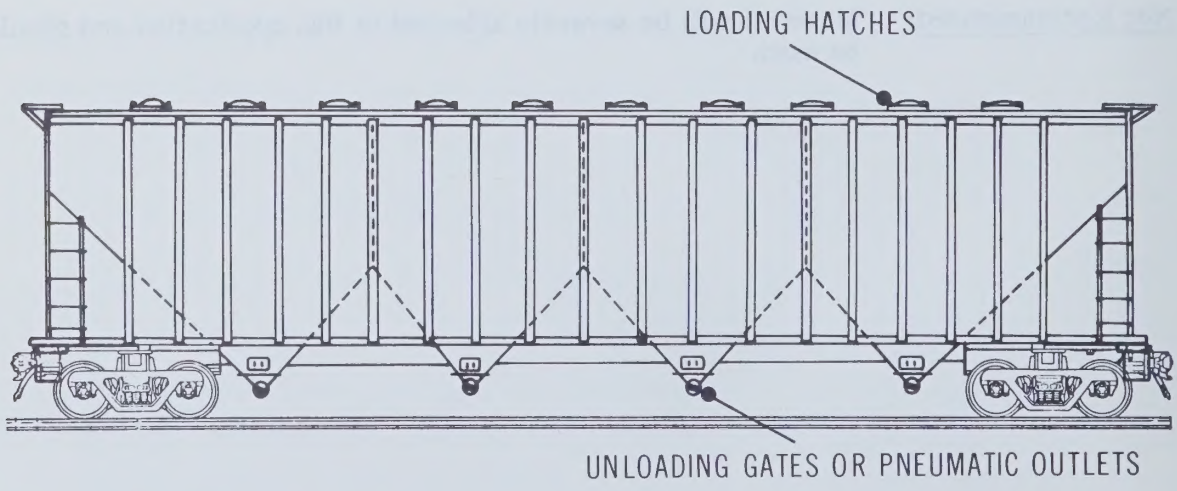
4.2 Compatibility with Materials of Construction. The compatibility of calcium oxide/hydroxide with materials of construction is indicated in Table 3. The unbracketed abbreviations are derived from Table 4. The rating system for this report is briefly described below.

Recommended:	This material will perform satisfactorily in the given application.
Conditional:	Material will show deterioration in the given application; however, it may be suitable for intermittent or short-term service.
Not Recommended:	Material will be severely affected in this application and should not be used.

(Reference - CLC 1974, AAR 1983)



Typical 3 - Compartment Hopper Car



Typical 4 - Compartment Hopper Car

TABLE 2 TYPICAL RAILWAY HOPPER CAR SPECIFICATIONS - AAR CLASS LO (CLC 1974)

Description	Hopper Car Size	
	5,800 (cu. ft)	4,700 (cu. ft)
Overall		
Nominal capacity	164 m^3 (5,800 cu ft)	133 m^3 (4,700 cu ft)
Weight capacity	89,000 kg (196,000 lb.)	86,000 kg (190,000 lb.)
Car weight - empty	45,000 kg (99,000 lb.)	45,000 kg (99,000 lb.)
Car weight - (max.)	119,000 kg (262,000 lb.)	119,000 kg (262,000 lb.)
Hoppers/Compartments		
Number	4	3
Material	Steel	
Inside length (typical)	410 cm (161 in.)	460 cm (181 in.)
Inside width (typical)	300 cm (118 in.)	300 cm (118 in.)
Spacing between outlets	4 m (13 ft)	5 m (16 ft)
Slope angle	40-45°	40-45°
Approximate Dimensions		
Coupled length	21 m (69 ft)	18 m (59 ft)
Length over strikers	20 m (66 ft)	17 m (56 ft)
Length of truck centers	16 m (52 ft)	14 m (46 ft)
Clearance height	5 m (16 ft)	5 m (16 ft)
Height to top of running board	5 m (16 ft)	4 m (13 ft)
Overall width	3.1 m (10 ft)	3.2 m (10.5 ft)
Inside length	19 m (62 ft)	17 m (56 ft)

Loading/Unloading Fixtures

Loading Hatches: Cars typically equipped with 4 to 12 loading hatches. Typical dimensions of these are 36-61 cm (14-24 in.) in diameter or square dimensions.

Unloading Fixtures: Equipped with unloading gates at bottom of 36-61 cm (14-24 in.) square or pneumatic unloading connections of 10-20 cm (4-8 in.) in diameter.

TABLE 3 COMPATIBILITY WITH MATERIALS OF CONSTRUCTION

Application	Chemical		Material of Construction		
	Conc.	Temp. (°C)	Recommended	Conditional	Not Recommended
1. Pipes and Fittings	Calcium Hydroxide (Saturated)	121	Chlorinated Polyether (DCRG 1978)		
		107	PP (DCRG 1978)		
		135	PVDF (DCRG 1978)		
		79	PVDC (DCRG 1978)		
	Calcium Oxide	121	PVDF (DCRG 1978)		
		121	Chlorinated Polyether (DCRG 1978)		
		107	PP (DCRG 1978)		
		79	PVDC (DCRG 1978)		
2. Valves	Calcium Hydroxide 10%	20	SS 316 (JSSV 1979)		
	10%	Boiling	SS 316 (JSSV 1979)		
3. Pumps	Calcium Hydroxide Suspensions		Body: All-Iron, Wetted Parts: Stainless Steel		
4. Storage			CS		

TABLE 3 COMPATIBILITY WITH MATERIALS OF CONSTRUCTION (cont'd)

Application	Chemical		Material of Construction		
	Conc.	Temp. (°C)	Recommended	Conditional	Not Recommended
5. Others	All	20	SS 316 SS 302 SS 304 SS 410 SS 430 (ASS)		
		Boiling	SS 316 (ASS)		SS 302 SS 304 (ASS)

TABLE 4 MATERIALS OF CONSTRUCTION

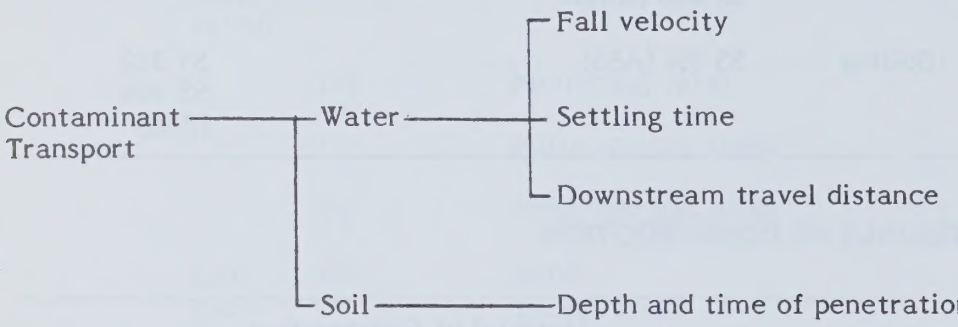
Abbreviation	Material of Construction
CS	Carbon Steel
	Cast Iron, Austenitic
	Chlorinated Polyether
FPM	Fluorine Rubber (Viton)
	Natural Rubber
	Nickel-Copper Alloy (Monel)
PP	Polypropylene
PVDC	Polyvinylidene Chloride (Saran)
PVDF	Polyvinylidene Fluoride (Kynar)
SS (Followed by Grade)	Stainless Steel

5 CONTAMINANT TRANSPORT

5.1 General Summary

Calcium oxide (quicklime) and calcium hydroxide (hydrated lime) are normally shipped and stored as solids. Calcium hydroxide is a fine, white powder which sinks in water. Due to its low solubility in water, it does not present a serious problem for either surface or groundwater contamination. Also, dispersion in air is not a problem.

Factors considered for a calcium hydroxide spill include:



It is important to note that, because of the approximate nature of the contaminant transport calculations, the approach adopted throughout has been to use conservative estimates of critical parameters so that predictions are approaching worst case scenarios for each medium. This may require that the assumptions made for each medium be quite different and, to some extent, inconsistent. As well as producing worst case scenarios, this approach allows comparison of the behaviours of different chemicals under consistent assumptions.

5.2 Leak Nomograms

Calcium oxide and calcium hydroxide are almost always carried as a solids in bulk or in bags. Lime suspensions are rarely shipped in bulk in railway tank cars or tank motor vehicles. Consequently, no leak nomograms have been prepared for this material.

5.3 Dispersion in the Air

Because calcium oxide/hydroxide is nonvolatile in spill circumstances, there is no significant potential for dispersion in the air other than in dust form.

5.4 Behaviour in Water

5.4.1 Introduction. When spilled on a water surface, calcium oxide (CaO) sinks and reacts violently with the water, producing heat and calcium hydroxide ($Ca(OH)_2$).

Calcium hydroxide (hydrated lime) is a fine white powder which sinks in water. It is only slightly soluble and does not normally represent a serious water pollution hazard.

To estimate the zone of contamination on a river bed resulting from a spill of an insoluble, high density solid on water, the terminal fall velocities (V_t) of the discrete particles have been estimated using a mathematical model (Thibodeaux 1980). The fall velocity of an individual particle is a function of its specific gravity, size, and cross-sectional area, together with the density and viscosity of water. The drag force (tending to resist fall of the particle through water) varies for different flow regimes. Details of the model are outlined in the Introduction Manual.

Based on available data (Domtar PDS 1980b), 96 percent by weight of calcium hydroxide powder is smaller than 0.3 mm in diameter, and 80 percent is less than 0.045 mm. The smallest particles are probably less than 0.005 mm in diameter. These will have very low terminal velocities (<0.001 cm/s) and will tend to remain in suspension indefinitely even with minimal stream turbulence.

5.4.2 Nomograms. The following nomograms are presented to estimate the extent of the downstream zone of contamination on a river bed following a spill of calcium hydroxide:

Figure 2: particle diameter versus terminal fall velocity

Figure 3: settling time versus terminal fall velocity for a range of stream depths

Figure 4: downstream distance versus settling time for a range of average stream velocities

5.4.2.1 Figure 2: Particle diameter versus terminal fall velocity. The terminal fall velocity (V_t) of discrete particles of calcium hydroxide in water can be estimated from Figure 2 for a given equivalent particle diameter, d.

5.4.2.2 Figure 3: Settling time versus terminal fall velocity. For a given particle size with terminal fall velocity (V_t), the time (t) to settle to the bottom of a river of depth (d), neglecting any turbulent mixing effects, can be estimated from Figure 3.

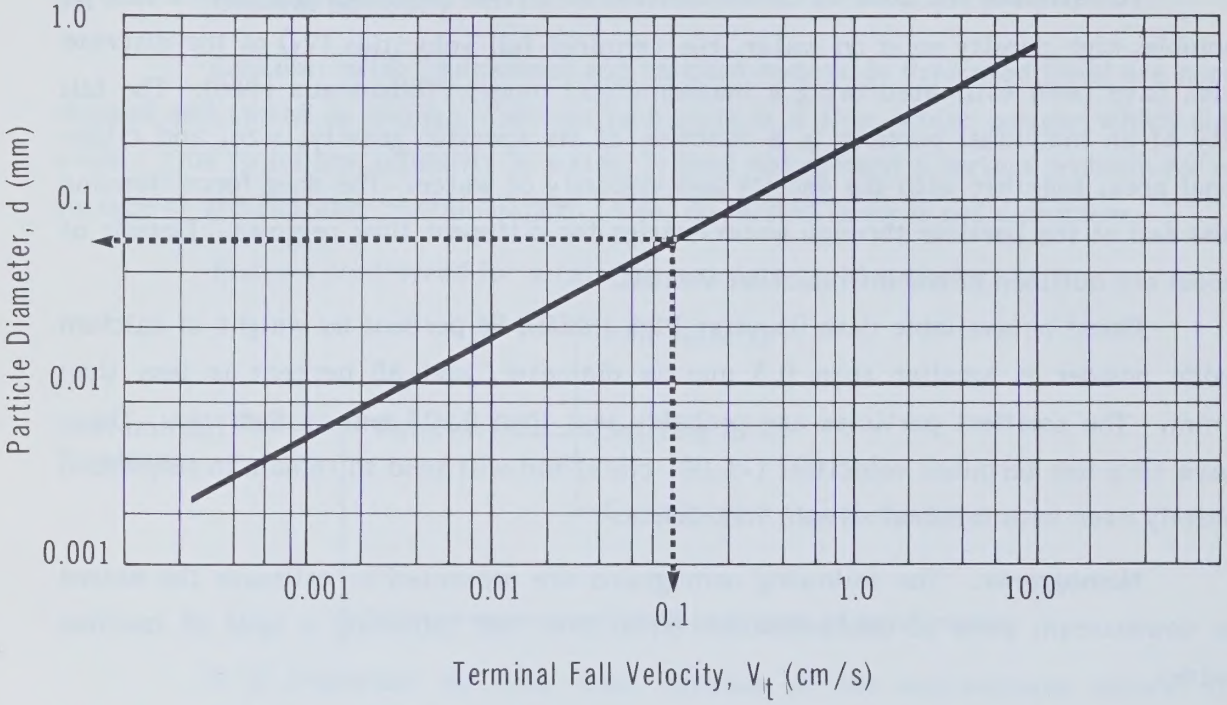
5.4.2.3 Figure 4: Downstream distance versus settling time. Based on the settling time derived from Figure 3, the downstream distance (X) at which the given particle size will reach the river bed can be determined from Figure 4 for a range of average stream velocities.

5.4.3 Sample Calculations. A 20 tonne spill of calcium hydroxide powder has occurred in a river. The stream depth is 5 m and the average stream velocity is 1 m/s.

FIGURE 2

CALCIUM OXIDE and HYDROXIDE

PARTICAL DIAMETER VS TERMINAL FALL VELOCITY



How far downstream will a discrete particle 0.06 mm in diameter be carried before reaching the stream bed? Neglect the effect of stream turbulence.

Solution

Step 1: Define terminal fall velocity (V_t)

- Use Figure 2
- With d = 0.06 mm, the terminal fall velocity is 0.1 cm/s

Step 2: Determine time for particle to settle to river bed

- Use Figure 3
- With V_t = 0.1 cm/s, and for a stream depth of 5 m, the settling time is 83 min

Step 3: Determine downstream distance

- Use Figure 4
- With t = 83 min and stream velocity (V) = 1 m/s, the downstream travel distance (X) of a particle 0.06 mm in diameter is 5,000 m (5 km).

FIGURE 3

CALCIUM OXIDE and HYDROXIDE

SETTLING TIME VS TERMINAL FALL VELOCITY

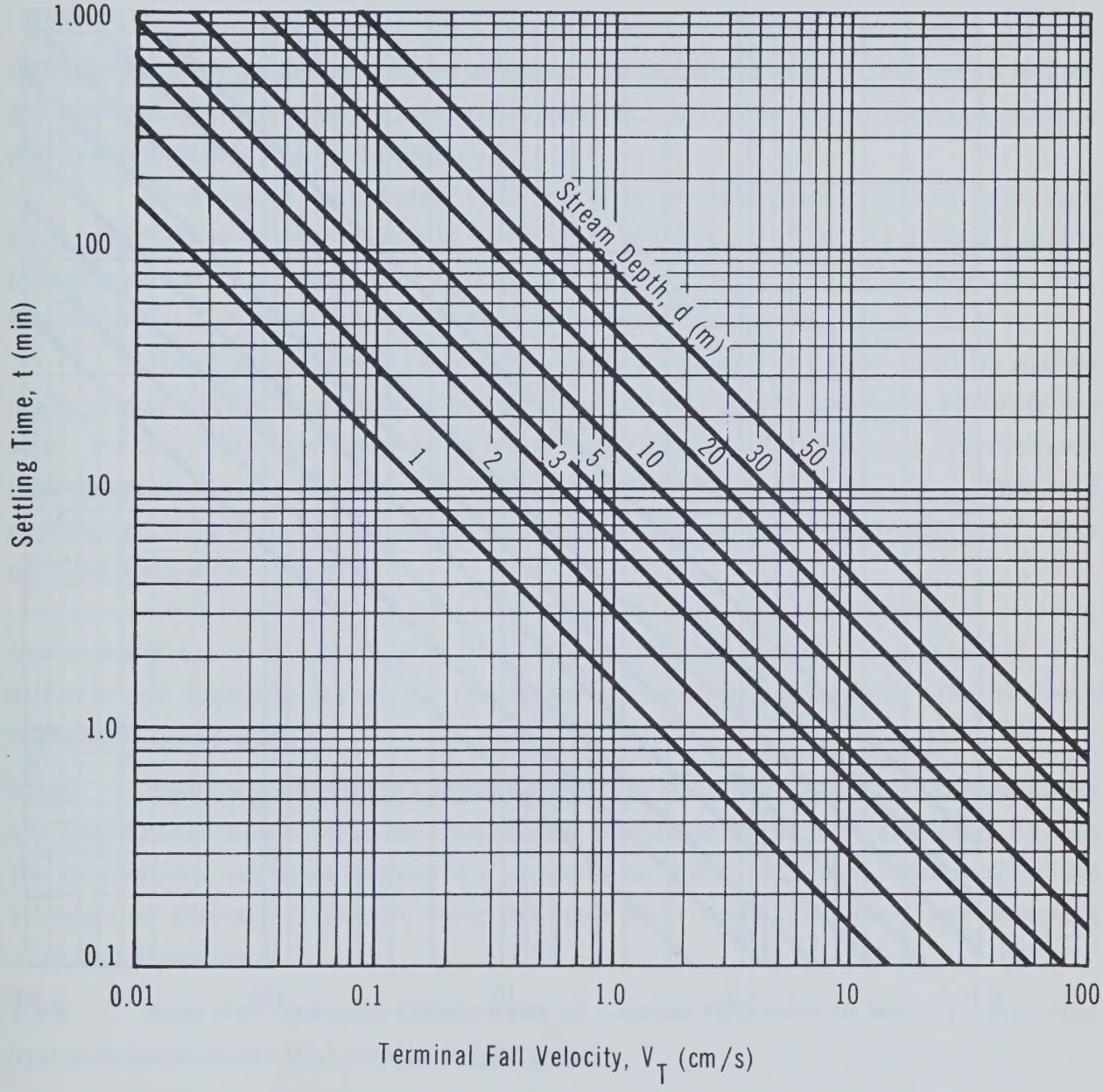
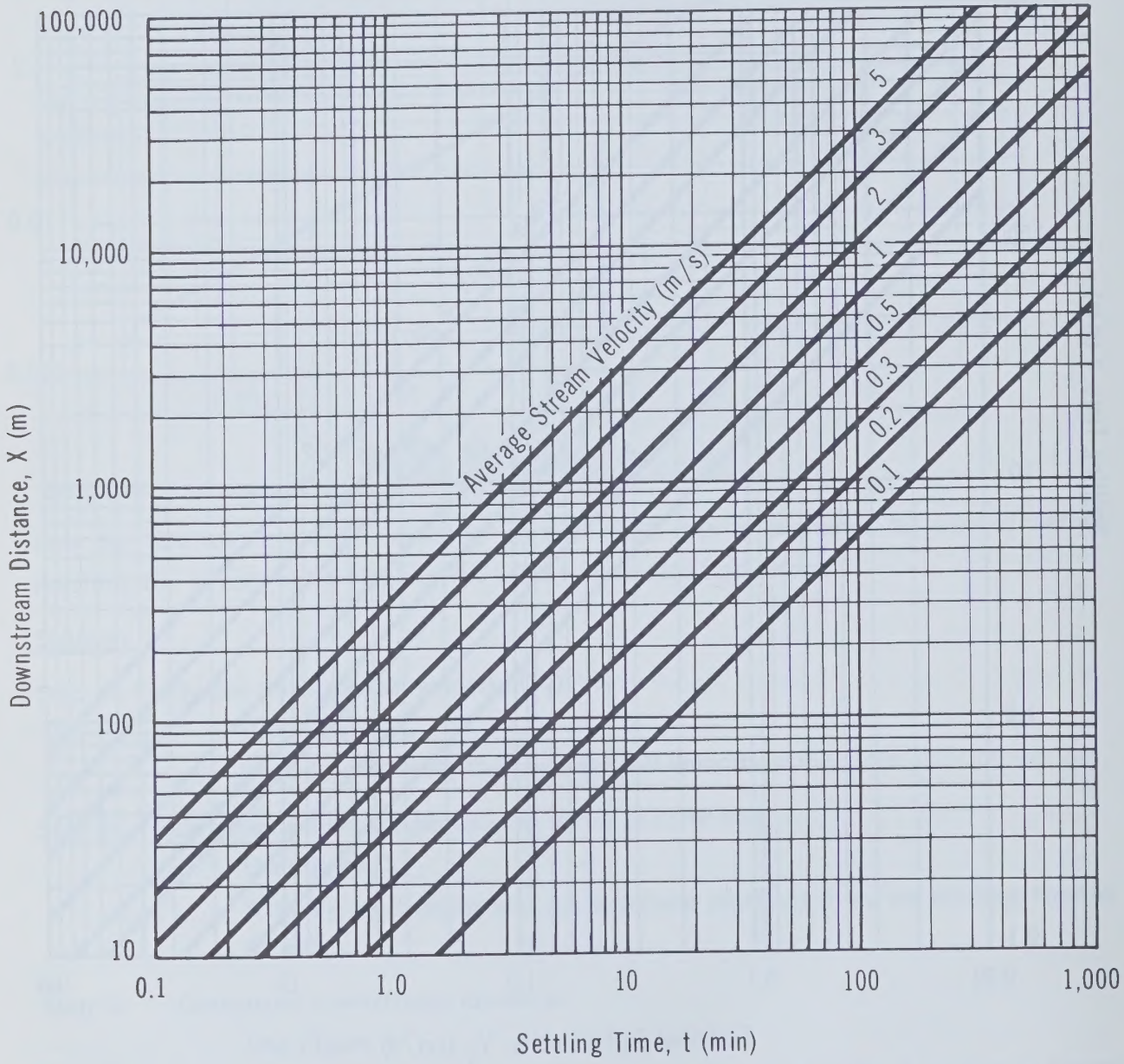


FIGURE 4

CALCIUM OXIDE and HYDROXIDE

DOWNSTREAM DISTANCE VS SETTLING TIME



5.5 Subsurface Behaviour: Penetration into Soil

5.5.1 Mechanisms. The principles of contaminant transport in soil and their application to this work are presented in the Introduction Manual. Special considerations related to the spill of calcium oxide/hydroxide onto soil and its transport downward through the soil are presented here.

Calcium oxide (CaO, quicklime) and calcium hydroxide ($Ca(OH)_2$, hydrated lime) are normally shipped and stored as solids. Consequently, when spilled, only a limited groundwater contamination hazard exists provided that the soil is dry and that no precipitation occurs prior to cleanup.

When mixed with water, CaO reacts to produce $Ca(OH)_2$ and evolves much heat. $Ca(OH)_2$ is slightly soluble in water (0.17 g/100 g at 0°C). As a result, in the presence of water, a contaminant solution will be produced which can infiltrate the soil. Runoff into surface water will occur if the soil surface is saturated.

The situation covered in the work deals with a spill of CaO or $Ca(OH)_2$ and the production of a dilute solution (0.1 percent by weight) of $Ca(OH)_2$ which can infiltrate the soil. The soils have been assumed to be at field capacity. This situation provides very little interstitial water to dilute the chemical during transport or to impede its downward movement. Interactions such as ion exchange in the soil have been neglected. This provides a worst case analysis.

Upon reaching the groundwater table, the contaminant will continue to move, now in the direction of groundwater flow. A contaminated plume will be produced, with diffusion and dispersion serving to reduce the concentration somewhat. This is shown schematically in Figure 5.

5.5.2 Equations Describing Calcium Hydroxide Movement into Soil. The equations and assumptions used to describe contaminant movement in solution downward through the unsaturated soil zone toward the groundwater table have been described in the Introduction Manual. Transport velocities have been based on Darcy's Law assuming saturated piston flow.

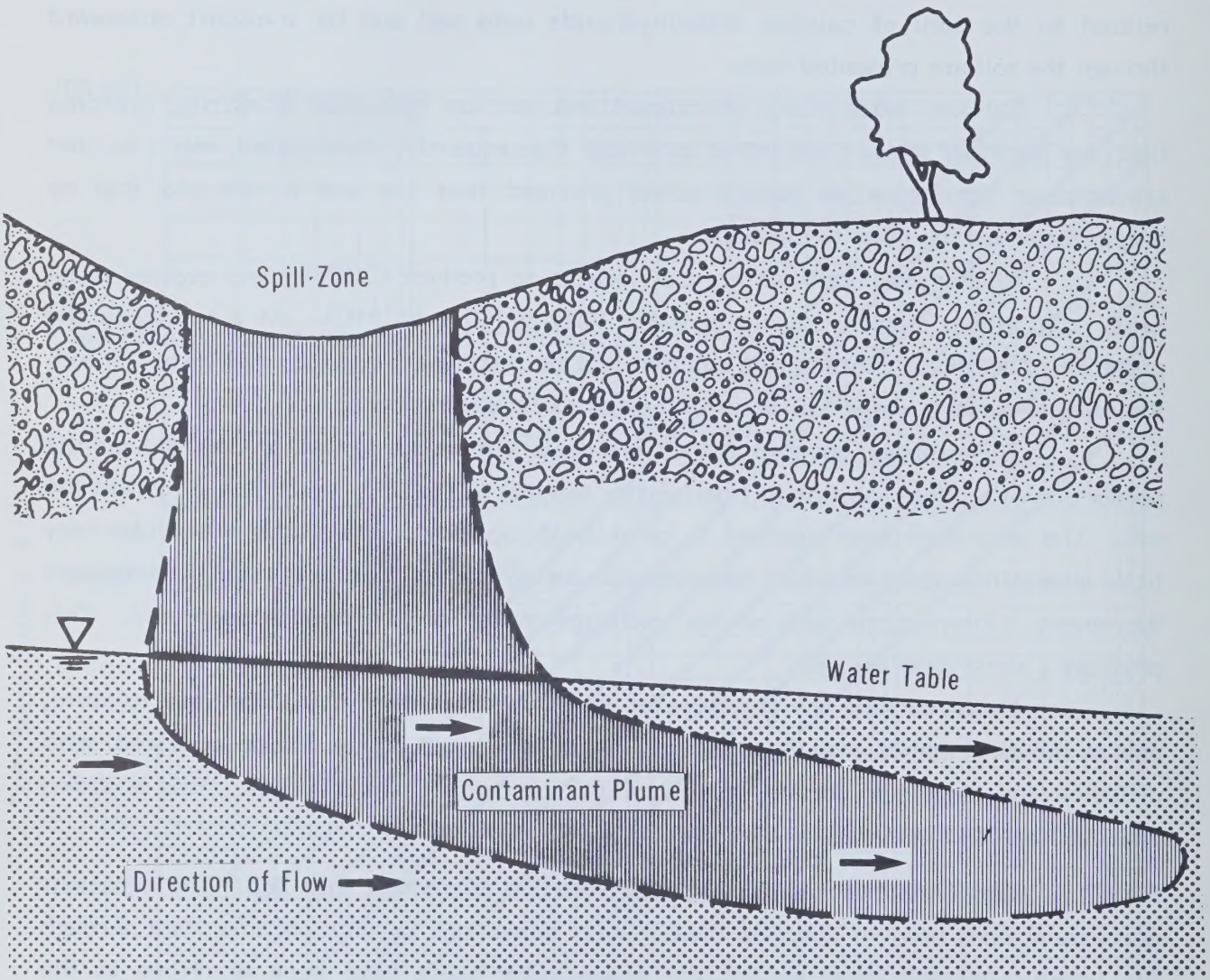
5.5.3 Saturated Hydraulic Conductivity of Calcium Hydroxide in Soil. The saturated hydraulic conductivity (K_o), in m/s, is given by:

$$K_o = \frac{(\rho g)k}{\mu}$$

FIGURE 5

CALCIUM OXIDE and HYDROXIDE

SCHEMATIC SOIL TRANSPORT



Soil: Coarse Sand

–Porosity (n) = 0.35

–Intrinsic Permeability (k) = 10^{-9} m^2

–Field Capacity (θ_{fc}) = 0.075

where:

k = intrinsic permeability of the soil (m^2)

ρ = mass density of the fluid (kg/m^3)

μ = absolute viscosity of the fluid (Pa•s)

g = acceleration due to gravity = 9.81 m/s^2

The fluids involved are calcium hydroxide, 0.1 percent by weight, and water. The water calculations represent the extreme as the solution is diluted.

Property	Calcium Hydroxide (0.1%) 20°C	Calcium Hydroxide (0.1%) 4°C	Water 20°C
Mass density (ρ), kg/m^3	998	1,000	998
Absolute viscosity (μ), Pa•s	1.01×10^{-3}	1.57×10^{-3}	1.0×10^{-3}
Saturated hydraulic conductivity (K_o), m/s	$(0.98 \times 10^7)k$	$(0.65 \times 10^7)k$	$(0.98 \times 10^7)k$

Calcium hydroxide (0.1 percent) has essentially the same hydraulic conductivity as water.

5.5.4 Soils. The Introduction Manual describes the three soils selected for this work. Their relevant properties are:

Property	Soil Type: Coarse Sand	Silty Sand	Clay Till
Porosity (n), m^3/m^3	0.35	0.45	0.55
Intrinsic permeability (k), m^2	10^{-9}	10^{-12}	10^{-15}
Field capacity (θ_{fc}), m^3/m^3	0.075	0.3	0.45

5.5.5 Penetration Nomograms. Nomograms for the penetration of calcium hydroxide into the unsaturated zone above the groundwater table were prepared for each soil. They present penetration time (t_p) plotted against depth of penetration (B). Because of the methods and assumptions used, the penetration depth should be considered as a maximum depth in time t_p.

A flow chart for the use of the nomograms is presented in Figure 6. The nomograms are presented as Figures 7, 8, and 9. The water line on the nomograms represents the maximum penetration of water at 20°C in time t_p. It is a limiting condition as the solution becomes diluted with water.

5.5.6 Sample Calculation. A 20 tonne spill of calcium hydroxide has occurred on coarse sand. The temperature is 20°C; the spill radius is 8.6 m. During cleanup, it begins to rain. Calculate the depth of penetration 20 minutes after the spill.

Solution

Step 1: Define parameters

- Mass spilled = 20,000 kg (20 tonnes)
- T = 20°C
- r = 8.6 m
- Soil = coarse sand
- Groundwater table depth (d) = 13 m
- Time since spill (t_p) = 20 min

Step 2: Calculate area of spill

- $A = \pi r^2 = 232\ m^2$

Step 3: Estimate depth of penetration (B) at time (t_p)

- For coarse sand at t_p = 20 min, 0.1 percent $Ca(OH)_2$, from Figure 7, B = 11.9 m
- Groundwater table has not been reached in this time

FIGURE 6

CALCIUM OXIDE and HYDROXIDE

FLOWCHART FOR NOMOGRAM USE

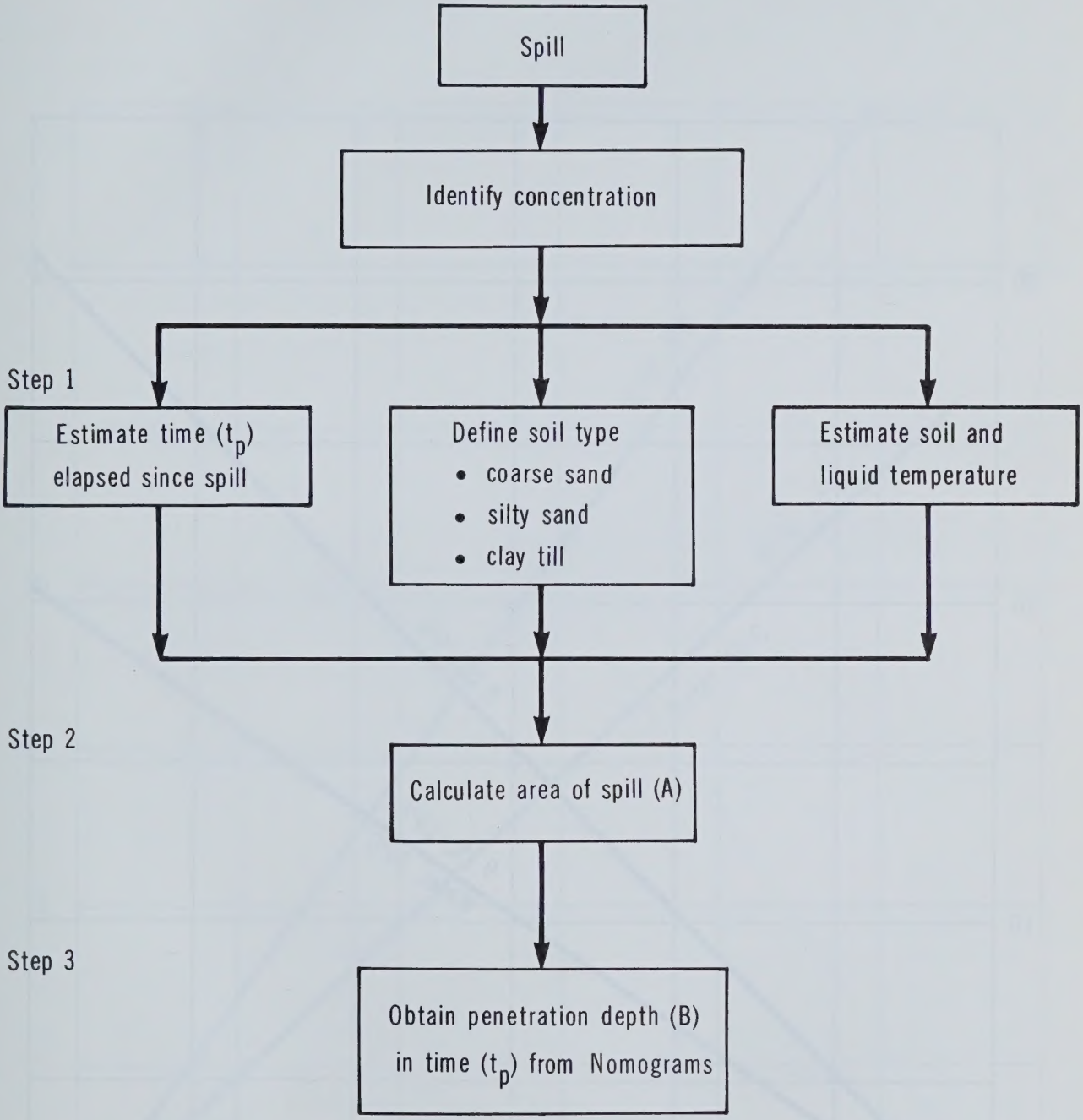


FIGURE 7

CALCIUM OXIDE and HYDROXIDE

PENETRATION IN COARSE SAND

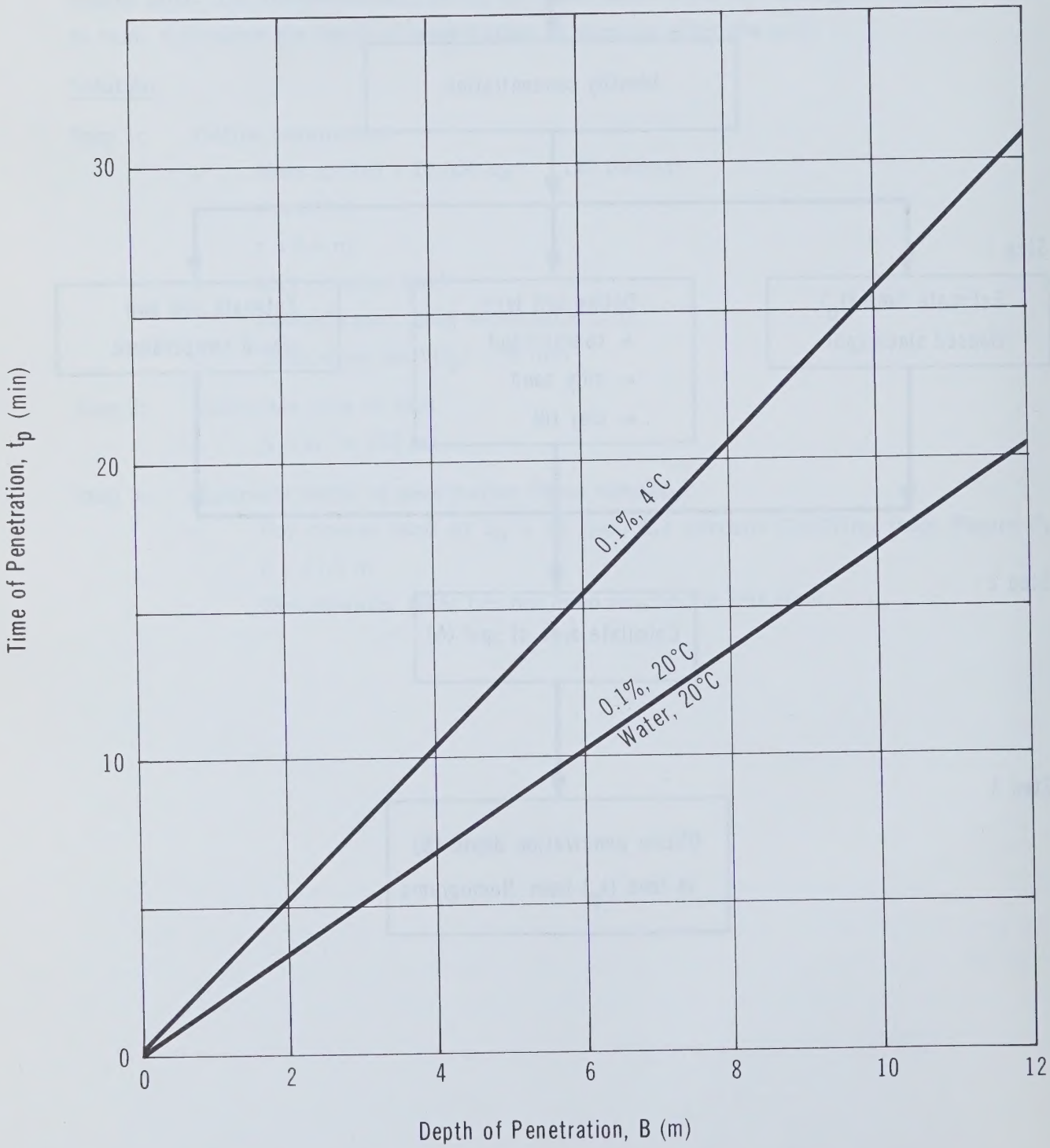


FIGURE 8

CALCIUM OXIDE and HYDROXIDE

PENETRATION IN SILTY SAND

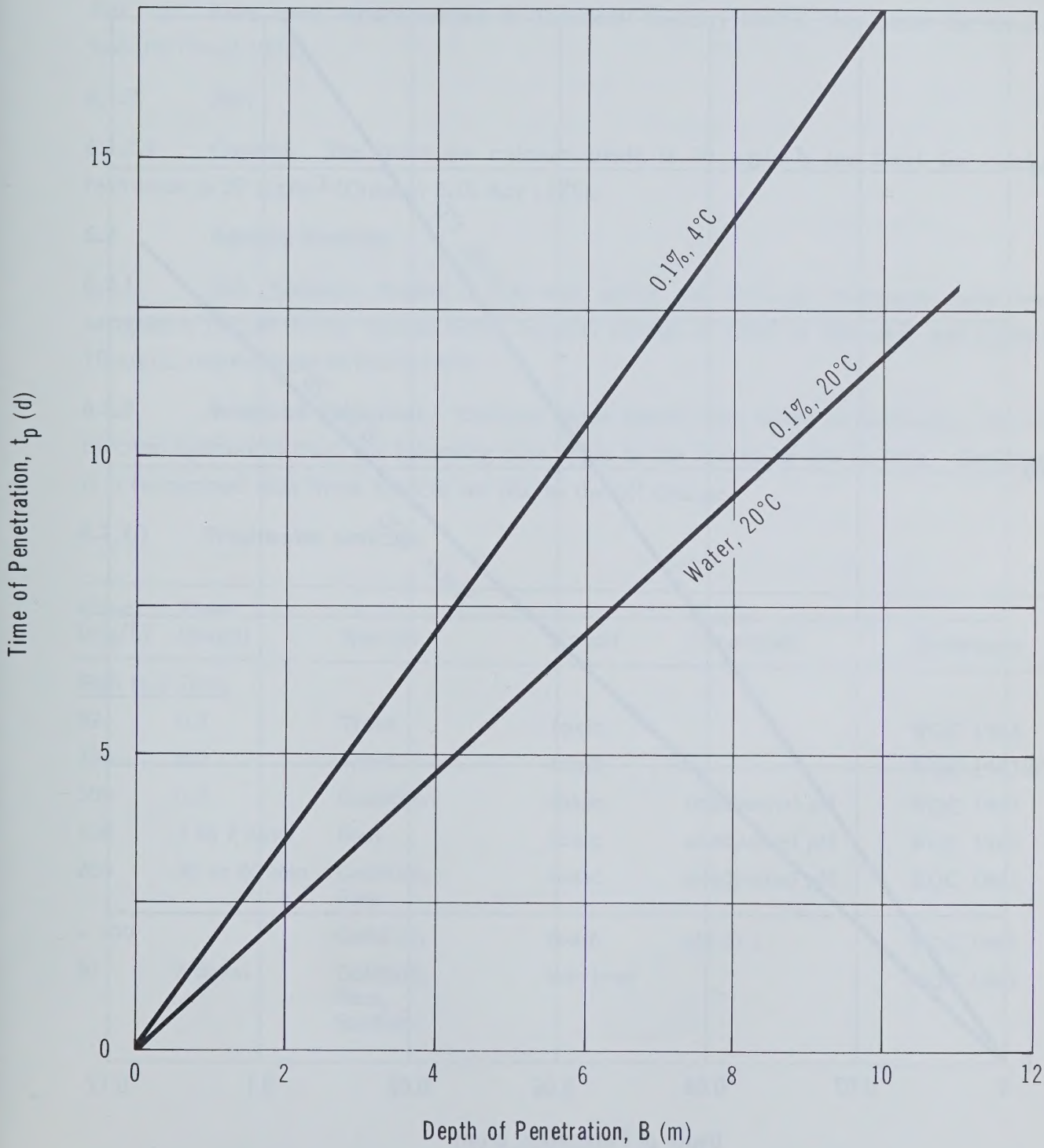
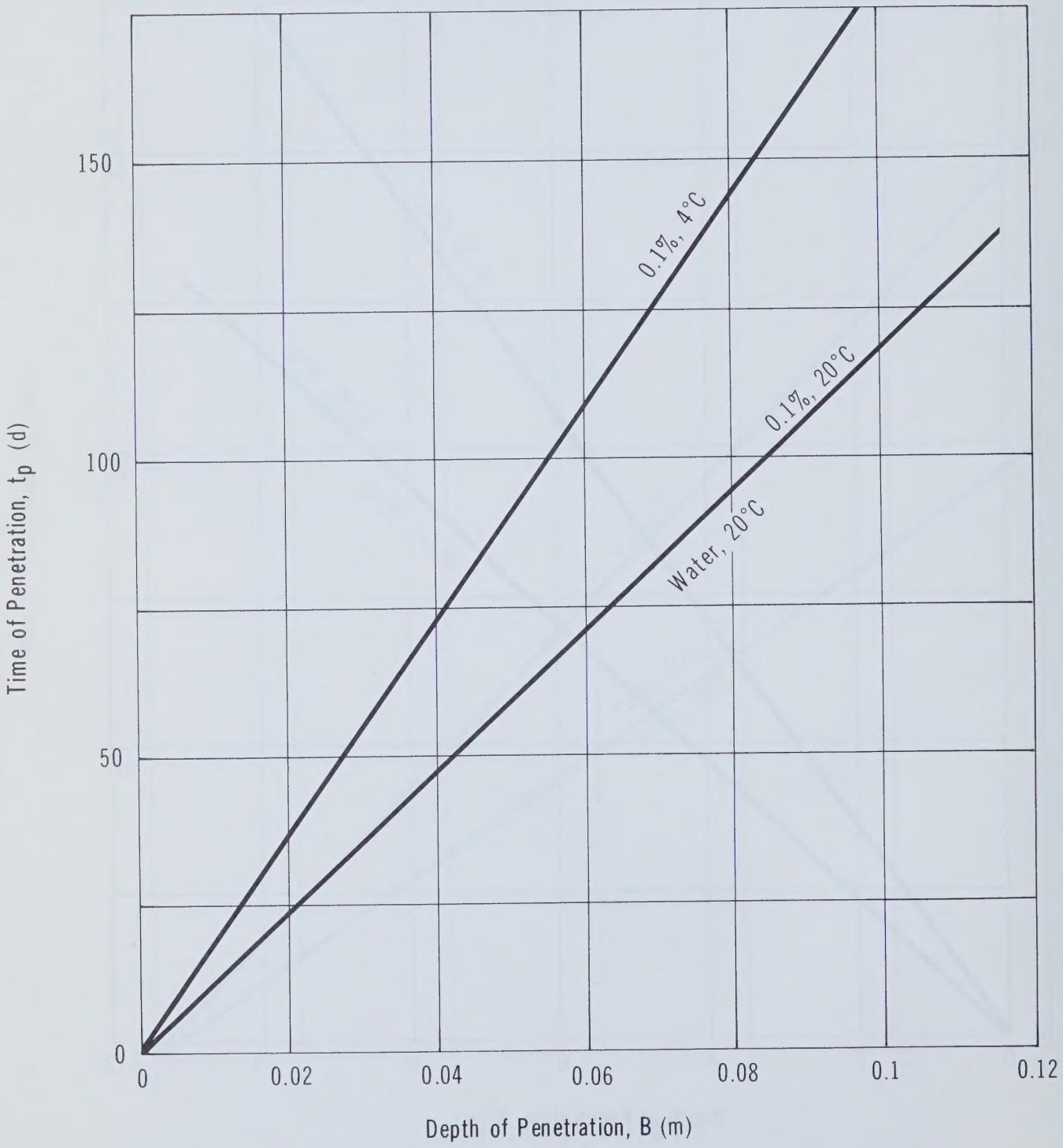


FIGURE 9

CALCIUM OXIDE and HYDROXIDE

PENETRATION IN CLAY TILL



6 ENVIRONMENTAL DATA

6.1 Suggested or Regulated Limits

6.1.1 Water. Not available. Drinking water standards based on acidity recommend that the pH be within the range of 6.5 to 8.5 (Water Management Goals 1978). 1,000 and 500 mg/L have been recommended as livestock toxicity limits, the latter for chronic toxicity (Todd 1970).

6.1.2 Air.

6.1.2.1 Canada. The limit for calcium oxide is 20 $\mu g/m^3$; the limit for calcium hydroxide is 27 $\mu g/m^3$ (Ontario E.P. Act 1971).

6.2 Aquatic Toxicity

6.2.1 U.S. Toxicity Rating. Calcium oxide and calcium hydroxide have been assigned a TL_m96 (4-day median lethal toxicity rating) of 1,000 to 100 mg/L and 1,000 to 10 mg/L, respectively (RTECS 1979).

6.2.2 Measured Toxicities. Calcium oxide reacts with water immediately, forming calcium hydroxide; thus, the following data apply to the hydroxide and its ions. Generally, it is recognized that these effects are due to the pH change.

6.2.2.1 Freshwater toxicity.

Conc. (mg/L)	Time (hours)	Species	Result	Water Conditions	Reference
Fish Kill Data					
92	0.7	Trout	toxic		WQC 1963
198	0.2	Trout	toxic		WQC 1963
500	0.3	Goldfish	toxic	unadjusted pH	WQC 1963
100	3 to 7 days	Bass	toxic	unadjusted pH	WQC 1963
200	30 to 80 min	Goldfish, Bass	toxic	unadjusted pH	WQC 1963
< 100		Goldfish	toxic	pH 11.1	WQC 1963
50	7 days+	Goldfish, Bass, Sunfish	survived		WQC 1963

Conc. (mg/L)	Time (hours)	Species	Result	Water Conditions	Reference
Fish Toxicity Tests					
240	24	Mosquito fish	TL_m	Turbid, 21 to 23°C	Wallen 1957
220	48	Mosquito fish	TL_m	Turbid, 21 to 23°C	Wallen 1957
160	96	Mosquito fish	TL_m	Turbid, 21 to 23°C	Wallen 1957
Invertebrates					
300	24	Vector snails	killed	28°C	WQCDB-3 1971

6.3 Effect Studies

Aquatic toxicity is the function of an alkalinity effect. Addition of lime to soft water lakes increases biological activity, possibly by providing a carbon dioxide reservoir (WQC 1963).

6.4 Degradation

Calcium oxide and hydroxide do not degrade oxidatively; they are neutralized by acidic constituents in the atmosphere including carbon dioxide, sulphur dioxide and nitrogen oxides (OHM-TADS 1981).

6.5 Long-term Fate and Effects

These compounds show no bioaccumulation or food chain concentration toxicity potential.

7 HUMAN HEALTH

There is a limited amount of information in the published literature concerning the toxicological effects of test animal and human exposures to calcium oxide and calcium hydroxide. Much of the published information pertaining to the health effects of these chemicals deals with the irritant properties of the solid and dust forms. No information is available on the effects of calcium oxide or calcium hydroxide on reproduction, nor their mutagenicity or carcinogenicity. Little information is available on the effects of chronic exposures. Calcium oxide and calcium hydroxide have been reported in the EPA TSCA inventory. The data summarized here are representative of information in the literature.

The toxicological data summarized here have been extracted from reliable standard reference sources. It should be noted that some of the data are for chronic (long-term), low-level exposures and may not be directly applicable to spill situations.

7.1 Recommended Exposure Limits

The exposure standards for calcium hydroxide and calcium oxide are based upon their irritant properties. Canadian provincial guidelines generally are similar to those of USA-ACGIH, unless indicated otherwise.

Guideline (Time)	Origin	Recommended Level	Reference
Time-weighted Averages (TWA)			
Calcium Hydroxide:			
TLV® (8 h)	USA-ACGIH	5 mg/m^3	TLV 1981
	Netherlands	0.2 mg/m^3	ILO 1980
TWA Exposure Criteria	Ontario	2.5 mg/m^3 (proposed)	OML 1981
Calcium Oxide:			
TLV® (8 h)	USA-ACGIH	2 mg/m^3	TLV 1981
PEL (8 h)	USA-OSHA	5 mg/m^3	NIOSH/OSHA 1981
	Sweden	2 mg/m^3	Doc. TLV 1981
TWA Exposure Criteria	Ontario	1.5 mg/m^3 (proposed)	OML 1981

Guideline (Time)	Origin	Recommended Level	Reference
Short-term Exposure Limits (STEL)			
Calcium Hydroxide:	No data		
Short-term Inhalation Limit (STIL)			
Calcium Oxide:			
STIL (30 min)	Suggested	10 mg/m^3	CHRIS 1978
Other Human Toxicities			
Calcium Hydroxide:	No data		
Calcium Oxide:			
IDLH	USA-NIOSH	250 mg/m^3	NIOSH/OSHA 1981

7.2 Irritation Data

7.2.1 Skin Contact.

Exposure Level (and Duration)	Effects	Reference
SPECIES: Human		
Calcium Hydroxide	Solid will burn skin	CHRIS 1978
Calcium Oxide	Solid will burn skin	CHRIS 1978
Dust, concentration not specified (6 h)	Burning, erythema	Calnan 1981
Dust, concentration not specified (24 h)	Will cause a brown-black necrotic dry crust to form	Calnan 1981
Concentration not specified	May produce burns or dermatitis with desquamation and vesicular rash	USDHEW 1977

7.2.2 Eye Contact.

Exposure Level (and Duration)	Effects	Reference
SPECIES: Human		
Calcium Hydroxide	Solid will burn eyes	CHRIS 1978
Calcium Oxide	Solid will burn eyes	CHRIS 1978
SPECIES: Cattle		
Calcium Hyroxide	Immediate whitening of corneal stroma, more evident in cattle than in humans	TDB (on-line) 1981
SPECIES: Rabbit		
Calcium Hydroxide		
Concentration not specified (1 min)	Gradual decrease in mucopoly-saccharides of the cornea, reaching maximum at 24 hours. Normal levels not achieved after 3 months	TDB (on-line) 1981
Concentration not specified	Whitening of corneal stroma more evident in rabbits than in humans	TDB (on-line) 1981

7.3 Threshold Perception Properties

7.3.1 Odour.

Exposure Level (and Duration)	Effects	Reference
Calcium Hydroxide	Odourless	CHRIS 1978
Calcium Oxide	Odourless	CHRIS 1978

7.3.2 Taste.

Exposure Level (and Duration)	Effects	Reference
Calcium Hydroxide	Slightly bitter, alkaline taste (in concentrated aqueous solutions)	Merck 1976
Calcium Oxide	No data	

7.4 Long-term Studies

7.4.1 Inhalation.

Exposure Level (and Duration)	Effects	Reference
Acute Exposures		
SPECIES: Human		
Calcium Hydroxide		
-	Moderately caustic irritant to respiratory tract	Doc. TLV 1981
Calcium Oxide		
25 mg/m^3	Strong nasal irritation	Patty 1981
9 to 10 mg/m^3 (mixture of dusts containing CaO)	No observable irritation	Patty 1981
Duration Not Specified		
SPECIES: Human		
Calcium Oxide		
Concentration not specified	Inflammation of the respiratory passages, ulceration and perforation of the nasal septum, and pneumonia have been reported	Doc. TLV 1981

7.4.2 Ingestion.

Exposure Level (and Duration)	Effects	Reference
Acute Exposures		
SPECIES: Human		
Calcium Hydroxide	No data	
Calcium Oxide	No data	
SPECIES: Rat		
Calcium Hydroxide		
7,340 mg/kg	LD_{50}	RTECS 1979
11.4 to 4.83 g/kg	LD_{50} (single oral intubation)	Patty 1981
Calcium Oxide	No data	
Chronic Exposures		
SPECIES: Rat		
Calcium Hydroxide		
50 and 350 mg/L	Male rats given chemical in tap water were restless, aggressive and had reduced food intake at 2 months. At 3 months, decreased body weight, decreased counts for erythrocytes and phagocytes, decreased hemoglobin. Gross necropsy showed inflammation of small intestine and dystrophic changes in stomach, kidneys, liver	Patty 1981
Calcium Oxide	No data	

7.5 Symptoms of Exposure

General symptoms of exposure found in most information sources have not been specifically referenced. Only those of a more specific or unusual nature have their sources indicated.

7.5.1 Inhalation.

Calcium Hydroxide

1. Irritation of nose and throat.
2. Coughing, sneezing.
3. Lacrimation.
4. Inflammation of respiratory passages.
5. Chemical bronchitis (USDHEW 1977).
6. Perforation of nasal septum (USDHEW 1977).

Calcium Oxide

1. Irritation of nose and throat.
2. Sneezing.
3. Lacrimation.
4. Mucous membrane burns.
5. Ulceration of buccal mucosa (USDHEW 1977).
6. Ulceration and perforation of nasal septum (Doc. TLV 1981).
7. Bronchitis (NIOSH/OSHA 1981).
8. Pneumonia (Doc. TLV 1981).
9. Risk of acute pulmonary edema (Lefèvre 1980).

7.5.2 Ingestion.

Calcium Oxide

1. Immediate, intense burning sensation in mouth, throat, and stomach.
2. Immediate effect on buccal (cheeks and mouth cavity) membranes, which become white.
3. Intense pain in swallowing.
4. Edema of the glottis (Lefèvre 1980).
5. Strong salivation, which increases the pain.
6. Vomiting; vomit is brown and contains pieces of mucous membrane of the stomach (digestive hemorrhage) (Lefèvre 1980).
7. Stomach cramps.
8. Rapid breathing.
9. State of shock.
10. Diarrhea, possibly blood-stained.
11. Risk of perforation of stomach.

12. Loss of consciousness.

Calcium Hydroxide

1. Burning sensation in mouth, esophagus, and stomach.
2. Irritation of mouth.
3. Pain in swallowing (Lefèvre 1980).
4. Stomach cramps.

7.5.3 Skin Contact.

Calcium Hydroxide

1. Skin irritation.
2. Dermatitis with desquamation and vesicular rash (USDHEW 1977).

Calcium Oxide

1. Skin irritation.
2. Dermatitis with desquamation and vesicular rash (USDHEW 1977).
3. Painful ulceration.
4. Profound, irreparable damage of tissues (Lefèvre 1980).
5. State of shock.

7.5.4 Eye Contact.

Calcium Hydroxide

1. Mechanical irritation, followed by chemical irritation (Lefèvre 1980).
2. Spasmodic blinking (USDHEW 1977).
3. Burns.
4. Ocular perforation (USDHEW 1977).

Calcium Oxide

1. Irritation.
2. Spasmodic blinking (USDHEW 1977).
3. Burns and irreparable damage of mucous membranes (Lefèvre 1980).
4. Ulceration of eyes (Lefèvre 1980).
5. Ocular perforation (USDHEW 1977).
6. Loss of sight.

8 CHEMICAL COMPATIBILITY

8.1 Compatibility of Calcium Oxide with Other Chemicals and Chemical Groups

SPECIFIC CHEMICAL OR CHEMICAL GROUP	HEAT GENERATION	FIRE	EXPLOSION	FORMATION OF FLAMMABLE GASES	VIOLENT POLYMERIZATION	DECOMPOSITION	FORMATION OF TOXIC FUMES	FORMATION OF SUBSTANCES OF GREATER TOXICITY	PRESSURIZATION IN CLOSED VESSELS	SOLUBILIZATION	VIOLENT REACTION	NON-HAZARDOUS REACTION	SPECIFICS	REFERENCE
GENERAL														
Water	•	•											May ignite combustible material	Bretherick 1979
SPECIFIC CHEMICALS														
Boron Trifluoride										•			Forms a fused mass	NFPA 1978
Chlorine Trifluoride		•								•				NFPA 1978
Ethanol	•	•											May ignite combustible material	Bretherick 1979
Fluoride	•													NFPA 1978
Hydrofluoric Acid										•				NFPA 1978
Phosphorus Pentoxide										•			Reacts violently with heat	Bretherick 1979

8.2 Compatibility of Calcium Hydroxide with Other Chemicals and Chemical Groups

SPECIFIC CHEMICAL OR CHEMICAL GROUP	HEAT GENERATION	FIRE	EXPLOSION	FORMATION OF FLAMMABLE GASES	VIOLENT POLYMERIZATION	DECOMPOSITION	FORMATION OF TOXIC FUMES	FORMATION OF SUBSTANCES OF GREATER TOXICITY	PRESSURIZATION IN CLOSED VESSELS	SOLUBILIZATION	VIOLENT REACTION	NON-HAZARDOUS REACTION	SPECIFICS	REFERENCE
SPECIFIC CHEMICALS														
Maleic Anhydride		•			•									NFPA 1978
Nitroethane		•											Form salts that are explosive when dry	NFPA 1978
Nitromethane		•											Form salts that are explosive when dry	NFPA 1978
Nitropropane		•											Form salts that are explosive when dry	NFPA 1978
Phosphorus			•											NFPA 1978
CHEMICAL GROUPS														
Nitroparaffins		•											Form salts that are explosive when dry	NFPA 1978

9 COUNTERMEASURES

9.1 Recommended Handling Procedures

The following procedures have been derived from a review of the literature. To avoid any deviation from the intended meaning, the wording of the original source has been presented essentially unchanged - in so doing, it is recognized that there may be some discrepancies between different sources of information. These procedures should not be considered as Environment Canada's recommendations.

9.1.1 Fire Concerns. Calcium oxide/hydroxide is a noncombustible material. Calcium oxide will swell and generate heat when moistened and could burst containers. Fluorine will attack calcium oxide, evolving much heat and some light (GE 1978).

Calcium hydroxide is a strongly alkaline material which is incompatible with acidic materials. In the presence of water, it reacts with nitroparaffins to form salts which are explosive when dried. It can cause the explosive decomposition of maleic anhydride. Boiling elemental phosphorus in a calcium hydroxide solution can liberate spontaneously flammable phosphines (GE 1978).

9.1.2 Fire Extinguishing Agents. Not combustible; in fires, use water in flooding amounts only (ERG 1980).

Small fires: Dry chemical, CO_2, water spray or foam.

Large fires: Water spray, fog or foam.

Move containers away from fire area if this can be done without risk (ERG 1980).

9.1.3 Spill Actions.

9.1.3.1 General. Stop or reduce discharge of material if this can be done without risk. Avoid skin contact and inhalation (GE 1978).

9.1.3.2 Spills on land. When spilled in a dry condition, the material can be shovelled into covered metal containers for recovery or disposal (avoid dusting and contact with skin) (GE 1978).

When spilled in a liquid condition, contain if possible by forming mechanical and/or chemical barriers to prevent spreading, and neutralize with vinegar or dilute acid (EPA 670/2-75-042). Sodium bicarbonate and carbon dioxide (best applied as a dilute solution) are recommended as in situ neutralizing agents (OHM-TADS 1981).

9.1.3.3 Spills on water. Contain if possible and neutralize with dilute acid (EPA 670/2-75-042). Strong acids would be effective providing that the response personnel are aware of the hazards. Sodium bicarbonate and carbon dioxide are recommended as in situ neutralizing agents (OHM-TADS 1981). Activated carbon may also be used to remove some material (CG-D-38-76). If not solubilized, an inert and sulphate-type cover material could be applied on the material in the water to prevent any additional solubilization of the spilled material (CG-D-56-78).

9.1.4 Cleanup and Treatment.

9.1.4.1 General. For treatment of contaminated water, the following procedure is recommended (EPA 600/2-77-227). The solids are removed by gravity separation and the (decant) water is neutralized (pH 7.0) with hydrochloric acid. The water is then treated with sodium carbonate to raise the pH to 9.0 and passed through dual media filtration. Prior to discharge, the water is neutralized with sulphuric acid (pH 7.0). Any wastewater from backwash of the filtration unit is returned to the gravity separator.

9.1.5 Disposal. Waste calcium oxide or hydroxide must never be discharged directly into sewers or surface waters. Following neutralization, either at the spill site or at a waste management facility, the resultant sludge can be disposed of in a secure landfill (OHM-TADS 1981; GE 1978).

9.1.6 Protective Measures. For entry into a situation where the spilled material and its characteristics are unknown, self-contained breathing apparatus and a totally encapsulated chemical suit should be worn.

If the spilled material is known to be calcium oxide/hydroxide:

- Response personnel should be provided with and required to use impervious clothing, gloves, face shields (20 cm minimum), and other appropriate protective clothing necessary to prevent skin contact with calcium oxide, where skin contact may occur (NIOSH/OSHA 1981).
- Dust-resistant or tight-fitting safety goggles are required for eye protection in dusty situations (NIOSH/OSHA 1981).
- Butyl has been recommended as a chemical suit material (excellent resistance) for protection against calcium oxide (EE-20).
- Nonimpervious clothing which becomes contaminated with calcium oxide should be removed promptly and not reworn until the calcium oxide is removed from the clothing (NIOSH/OSHA 1981).

The following is a list of the minimum respiratory protection recommended for personnel working in areas where calcium oxide is present (NIOSH/OSHA 1981).

Condition	Minimum Respiratory Protection* Required above 5 mg/m^3
Particulate Concentration	
25 mg/m^3 or less	Any dust and mist respirator.**
50 mg/m^3 or less	Any dust and mist respirator, except single-use or quarter-mask respirator.**
	Any supplied-air respirator.**
	Any self-contained breathing apparatus.**
250 mg/m^3 or less	A high efficiency particulate filter respirator with a full facepiece.
	Any supplied-air respirator with a full facepiece, helmet, or hood.
	Any self-contained breathing apparatus with a full facepiece.
Greater than 250 mg/m^3 or entry and escape from unknown concentrations	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode.
	A combination respirator which includes a Type C supplied-air respirator with a full facepiece operated in pressure-demand or other positive pressure or continuous-flow mode and an auxiliary self-contained breathing apparatus operated in pressure-demand or other positive pressure mode.
Fire Fighting	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode.
Escape	A high efficiency particulate filter respirator with a full facepiece.
	Any escape self-contained breathing apparatus.

* Only NIOSH-approved or MSHA-approved equipment should be used.

** If eye irritation occurs, full-facepiece respiratory protective equipment should be used.

- Eyewash stations and safety showers should be readily available in areas of use and in spill situations (GE 1978).

9.1.7 Special Precautions (Calcium Oxide). Store material in sealed containers in a dry place, away from acids and organic materials. Protect containers against physical damage. Remember that this material will generate heat by reaction with water; care should be taken to see that this heat is dissipated safely when it is deliberately mixed with water. If exposed to air, it will react with water and with carbon dioxide. Use due caution in mixing with water and handling the alkaline water dispersions of this material (milk of lime) (GE 1978).

10 PREVIOUS SPILL EXPERIENCE

Although spills of this material have been recorded, no significant information regarding cleanup methods or response has been documented.

11 ANALYTICAL METHODS

The general approach adopted for each of the Priority Chemicals was as follows.

Methods have been documented here for analyses of air, water and soil samples in a normally equipped chemical laboratory remote from the spill site. Customary sources of standard or recommended analytical methods were consulted, and outlines are presented for each chemical. These sources included publications of the U.S. National Institute for Occupational Safety and Health (NIOSH), the U.S. Environmental Protection Agency (EPA), the American Water Works Association (AWWA), the American Society for Testing and Materials (ASTM), and the American National Standards Institute (ANSI).

If the standard or recommended methods were judged to be reliable and specific enough for the analysis of environmental and materials samples from spill sites and if they do not require highly specialized laboratory equipment, no additional methods were sought.

If especially simple, reliable tests (e.g. commonly used industrial methods) were found, they have been presented as well.

The methods presented below for calcium oxide are also applicable for calcium hydroxide.

11.1 Quantitative Method for the Detection of Calcium Oxide in Air

11.1.1 Atomic Absorption (NIOSH 1977). A range of 2.6 to 10.16 mg/m^3 (1.13 to 4.43 ppm) of calcium oxide in air can be determined by atomic absorption spectroscopy. The method is not specific to calcium oxide and will be applicable for any acid-soluble calcium compound present.

A known volume of air is drawn through a three-piece cassette filter holder capable of holding 37 mm filters. The filters are 0.8 µm cellulose-ester membrane. A sample volume of 85 L is recommended at a flow rate of 1.5 L/min.

The sample is transferred to a beaker and treated with 5 mL of concentrated nitric acid and heated on a hot plate (140°C) with a glass cover until most of the acid has evaporated. This step must be conducted in a fume hood. A 2 mL volume of concentrated nitric acid is added as well as 1 mL of 60 percent perchloric acid and the beaker covered with a glass cover. The sample is then heated until dense fumes of perchloric acid appear. Distilled water is used to rinse the sides of the beaker and the solution is evaporated to dryness. The sample is allowed to cool and the residue dissolved in 5 mL dilute

(5.0 percent v/v) hydrochloric acid containing 1 percent lanthanum. The solution is quantitatively transferred to a 100 mL volumetric flask and two 5 mL rinsings of the beaker are also added to the flask. The volume is then taken to 100 mL with dilute hydrochloric acid solution containing 1 percent lanthanum.

The sample is aspirated into an oxidizing air acetylene flame. The absorbance at a wavelength of 422.7 nm is recorded using a suitable atomic absorption spectrophotometer. The calcium oxide is determined using a calibration curve.

11.2 Qualitative Method for the Detection of Calcium Oxide in Air

The sample is collected as in Section 11.1.1. A clean platinum wire is dipped in the sample and then held in the hottest part of a nonluminous bunsen burner flame. A brick-red flame indicates the presence of calcium. This test is not specific for calcium oxide (Welcher 1955).

11.3 Quantitative Method for the Detection of Calcium Oxide in Water

11.3.1 Atomic Absorption Spectroscopy (ASTM 1979). A range of 0.3 to 15 mg/L (ppm) of calcium (any soluble calcium present) in water may be determined using atomic absorption spectroscopy.

At least 2 L of water are collected in an appropriate container. The sample should be filtered prior to aspiration into an atomic absorption spectrophotometer if particulate matter is present. A 100 mL volume of sample is mixed with 25 mL of a 5.0 percent lanthanum solution prior to analysis. The sample is aspirated into an air-acetylene flame. The absorbance at a wavelength of 422.7 nm is recorded using a suitable atomic absorption spectrophotometer. The calcium is determined using absorbance values and a standard curve.

11.4 Qualitative Method for the Detection of Calcium Oxide in Water

The sample is collected as in Section 11.3.1. A clean platinum wire is dipped in the sample and then held in the hottest part of a nonluminous bunsen burner flame. A brick-red flame indicates the presence of calcium. This test is not specific for calcium oxide (Welcher 1955).

11.5 Quantitative Method for the Detection of Calcium Oxide in Soil

11.5.1 Colourimetric (Hesse 1972). A maximum of 25 µg of calcium in soil can be determined using a 1.0 g soil sample and colourimetry. High levels of calcium carbonate present in some soils may results in interference and thus background levels should also be measured.

A 1.0 g sample of 0.15 mm, oven dried soil is placed in a 250 mL beaker and 20 mL of concentrated nitric acid are added. The beaker is covered and carefully heated to oxidize the organic matter. A 10 mL volume of 60 percent perchloric acid is added and the mixture digested until dense fumes of perchloric acid appear. This procedure must be conducted in a fume hood. The sides of the beaker are washed with perchloric acid as necessary. The mixture is then evaporated until all excess of perchloric acid is gone.

A suitable aliquot of the soil extract is taken and transferred to a test tube. The aliquot is diluted to 10 mL with water. A 10 mL volume of absolute methanol is added as well as 1 mL of buffer solution. This is prepared by dissolving 0.20 g sodium diethyldithiocarbanate in 100 mL of stock buffer solution. The stock buffer solution is prepared by dissolving 5.28 g of sodium tetraborate in 800 mL water and adding 10 g sodium hydroxide. The mixture is allowed to cool then diluted to 1 L with water and stored in a polyethylene bottle. The pH of the buffer solution should be 12 and should be adjusted if necessary. To the sample is added a 0.5 mL volume of reagent solution prepared by dissolving 0.150 g glyoxal bis-(2-hydroxyanil) in 30 mL of absolute methanol. The colour is developed for 25 minutes and the absorbance read on a suitable spectrophotometer at a wavelength of 535 nm. The calcium is determined using absorbance values and a standard curve.

11.6 Qualitative Method for the Detection of Calcium Oxide in Soil

The sample is collected as in Section 11.5.1 and the acid digestion procedure followed. A clean platinum wire is dipped in the sample and a few drops of 6 M hydrochloric acid are added. The platinum wire is held in the hottest part of a non-luminous bunsen burner flame. A brick-red flame indicates the presence of calcium. This test is not specific for calcium oxide (Welcher 1955).

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EnviroTIPS

Common Abbreviations

BOD	biological oxygen demand
b.p.	boiling point
CC	closed cup
cm	centimetre
CMD	count median diameter
COD	chemical oxygen demand
conc.	concentration
c.t.	critical temperature
eV	electron volt
g	gram
ha	hectare
Hg	mercury
IDLH	immediately dangerous to life and health
Imp. gal.	imperial gallon
in.	inch
J	joule
kg	kilogram
kJ	kilojoule
km	kilometre
kPa	kilopascal
kt	kilotonne
L	litre
lb.	pound
LC_{50}	lethal concentration fifty
LC_{LO}	lethal concentration low
LD_{50}	lethal dose fifty
LD_{LO}	lethal dose low
LEL	lower explosive limit
LFL	lower flammability limit
m	metre
m	meta
M	molar
MAC	maximum acceptable concentration
max	maximum
mg	milligram
MIC	maximum immision concentration
min	minute or minimum
mm	millimetre
MMAD	mass median aerodynamic diameter
MMD	mass median diameter
m.p.	melting point
MW	molecular weight
N	newton
NAS	National Academy of Sciences
NFPA	National Fire Protection Association
NIOSH	National Institute for Occupational Safety and Health
nm	nanometre
o	ortho
OC	open cup
p	para
P_c	critical pressure
PEL	permissible exposure level
pH	measure of acidity/alkalinity
ppb	parts per billion
ppm	parts per million
P_s	standard pressure
psi	pounds per square inch
s	second
STEL	short-term exposure limit
STIL	short-term inhalation limit
T_c	critical temperature
TC_{LO}	toxic concentration low
T_d	decomposition temperature
TD_{LO}	toxic dose low
TL_m	median tolerance limit
TLV	Threshold Limit Value
T_s	standard temperature
TWA	time weighted average
UEL	upper explosive limit
UFL	upper flammability limit
VMD	volume mean diameter
v/v	volume per volume
w/w	weight per weight

µg	microgram
µm	micrometre
°Be	degrees Baumé (density)